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U.S. DEPARTMENT OF  
**ENERGY**

# **Predicting and Understanding Novel Electrode Materials from First-Principles**

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**Eric Sivonxay and Julian Self**

**Principal Investigator, Project ID BAT091**

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# Overview

## Timeline

- October 1<sup>st</sup> 2016 - September 30<sup>st</sup> 2019.
- Percent complete: 75%

## Budget

- Funding for FY 18: \$450K

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong

## Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

## Partners

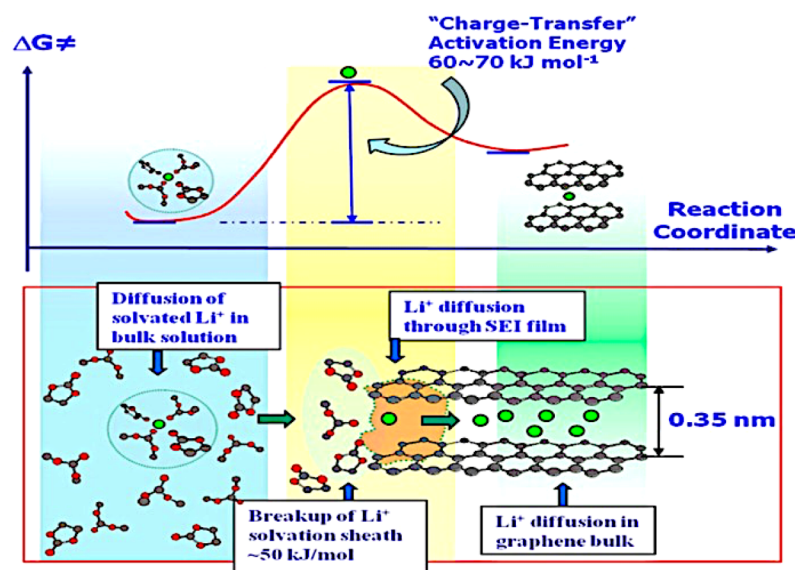
- NREL; Tony Burrell (SEista Program)
- Brett McCloskey (LBNL)
- Brett Lucht (University of Rhode Island )

# Milestones

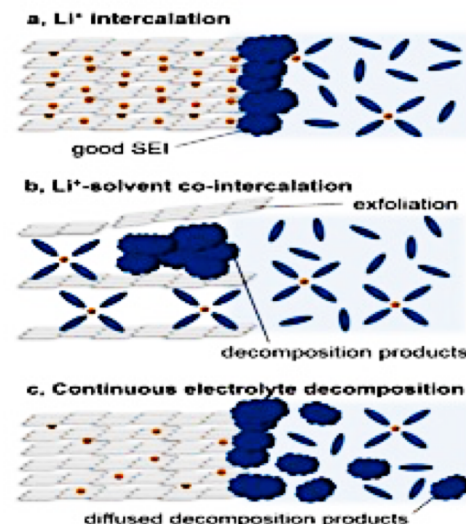
Month / Year	Milestone	Status
December 2017	Finish modeling of $\text{LiAsF}_6$ in weakly solvating solvent. Identification of concentration limit causing change in $\text{Li}^+$ solvation structure between contact-ion pair and solvent separated species.	Completed
March 2018	Finish modeling of $\text{LiPF}_6$ in weakly solvating solvent. Identification of concentration limit causing change in $\text{Li}^+$ solvation structure between contact-ion-pair and solvent separated species.	Completed
June 2018	Modeling of dielectric constant of complex $\text{Li}^+$ electrolytes using molecular dynamics.	Ongoing
September 2018	Present kinetic and thermodynamic evaluations of lithitation mechanisms of amorphous Si and $\text{SiO}_2$ .	Complete

# Relevance – The Organic Electrolyte Solvation Picture does not always set the performance limits of liquid electrolytes

## Chemical Reviews



**Figure 45.**  $\text{Li}^+$ -transport through interphase: (top) schematic illustration of solvated  $\text{Li}^+$  and bare  $\text{Li}^+$  intercalation at graphite edges and the corresponding activation energy barriers; (bottom) differentiation of the contributions from  $\text{Li}^+$ -desolvation and  $\text{Li}^+$ -migration across the interphase. Reprinted with permission from ref 577. Copyright 2010 American Chemical Society.

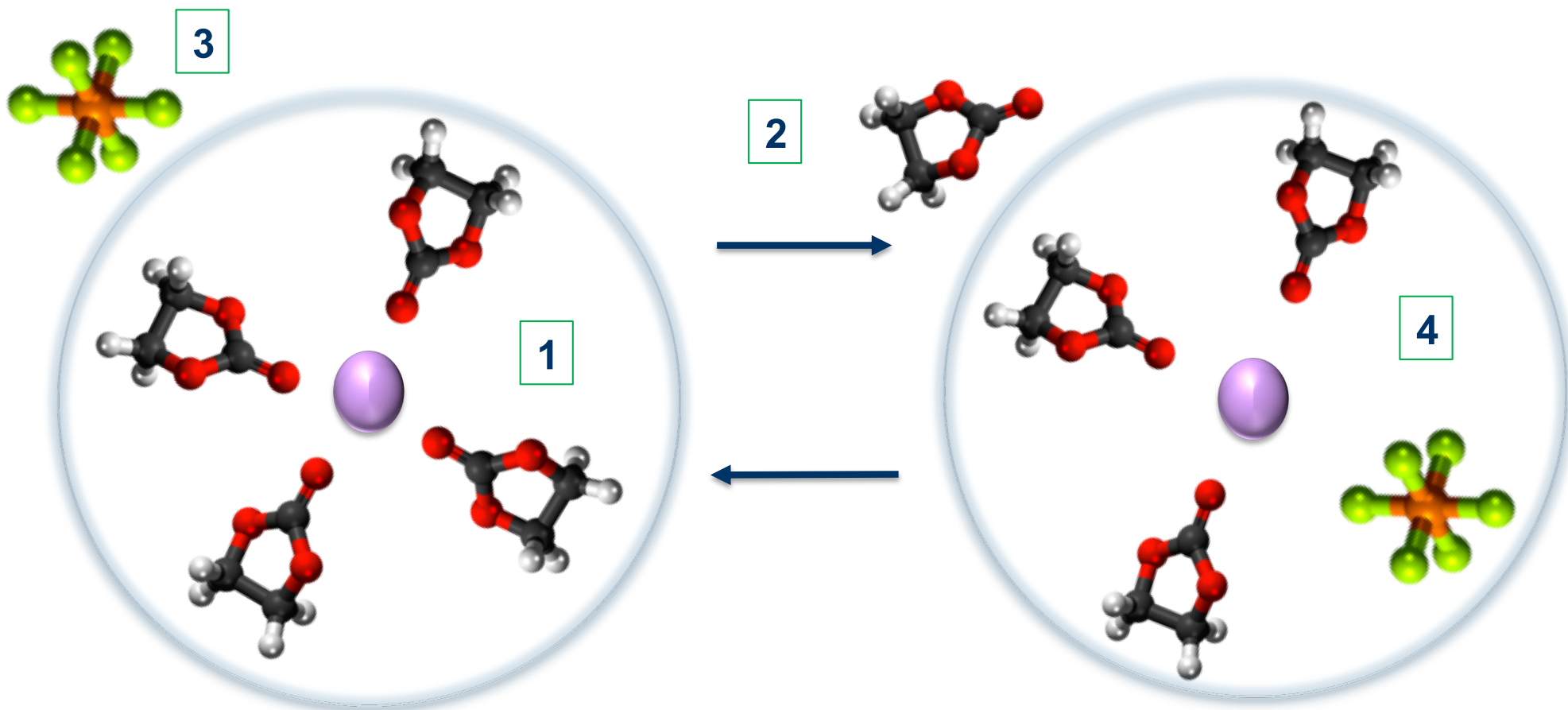


**Figure 8.** Three major scenarios of the reduction of graphite electrodes in  $\text{Li}$ -based electrolytes. a) Reversible  $\text{Li}^+$  intercalation as a result of good passivation (i.e., excellent SEI formation) by small amount of electrolyte decomposition. b)  $\text{Li}^+$ -solvent co-intercalation (i.e., intercalation of solvated  $\text{Li}^+$ ) sometimes accompanied with the exfoliation of graphene layers. c) Continuous electrolyte decomposition as a result of poor passivation because of low reductive stability of the electrolyte or high diffusivity of the decomposition products.

Typical solvation picture includes only the majority population such as well-solvated species. However, many of the performance-limiting properties (e.g. electrochemical window) of electrolytes comes from the variety of minority species, such as contact ion-pairs, complexes etc



## Relevance – Consider All Species Available; Sets different Limits



- Even at 1 M concentrations; contact ion-pairs exist in standard Li electrolytes
- Impact on transport as well as reduction/oxidation mechanisms
- Imperative to consider if we are to achieve improved understanding and ‘bottoms-up’ molecular design of electrolytes

# Relevance – The Case for Low Permittivity Li-ion Electrolytes

*Journal of The Electrochemical Society*, **164** (1) A5008-A5018 (2017)

FOCUS ISSUE OF SELECTED PAPERS FROM IMLB 2016 WITH INVITED PAPERS CELEBRATING 25 YEARS OF LITHIUM ION BATTERIES

## A Guide to Ethylene Carbonate-Free Electrolyte Making for Li-Ion Cells

Lin Ma,<sup>a,\*</sup> S. L. Glazier,<sup>b</sup> R. Petibon,<sup>a</sup> Jian Xia,<sup>b,\*</sup> Jeremy M. Peters,<sup>b</sup> Q. Liu,<sup>b,c</sup> J. Allen,<sup>b</sup> R. N. C. Doig,<sup>d</sup> and J. R. Dahn<sup>a,b,\*,z</sup>

<sup>a</sup>Department of Chemistry, Dalhousie University, Halifax B3H 4R2, Canada

<sup>b</sup>Department of Physics and Atmospheric Science, Dalhousie University, Halifax B3H 3J5, Canada

<sup>c</sup>MIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

<sup>d</sup>Department of Mathematics and Statistics, Dalhousie University, Halifax B3H 4R2, Canada

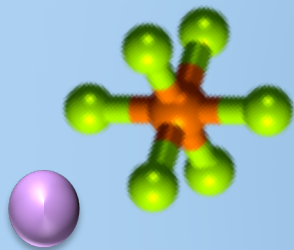
Linear carbonates:

Pros: higher anodic stability  
(good cyclability)

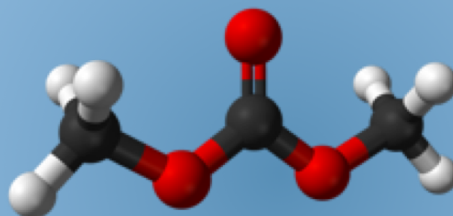
Cons: moderate transport,  
SEI formation

EC is important for SEI  
formation, but can be used  
as an additive

SALT:

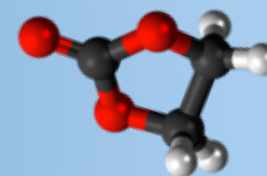


SOLVENT:



Linear Carbonate  
 $\epsilon = 3.1$  (25 C)

ADDITIVE:



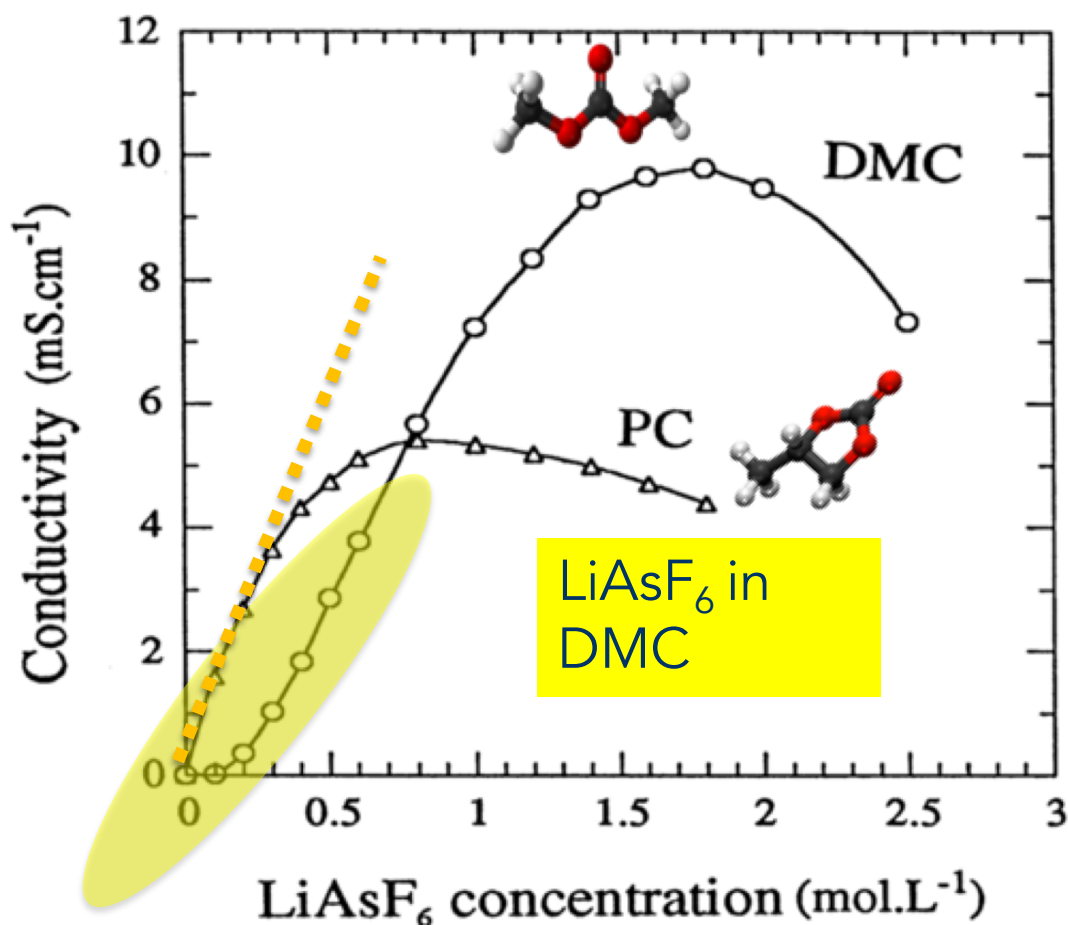
Cyclic Carbonate  
 $\epsilon = 90$  (40C)  
2% w.t.

A. J. Gmitter, I. Plitz, and G. G. Amatucci, *J. Electrochem. Soc.*, **159**, A370 (2012).

R. Petibon, J. Xia, L. Ma, M. Bauer, K. Nelson, and J. R. Dahn, *J. Electrochem.*

*Soc.*, **163**, A2571 (2016).

# Relevance – Non-linear conductivity at dilute concentrations?

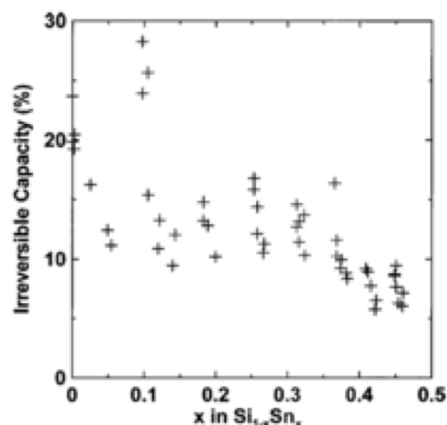
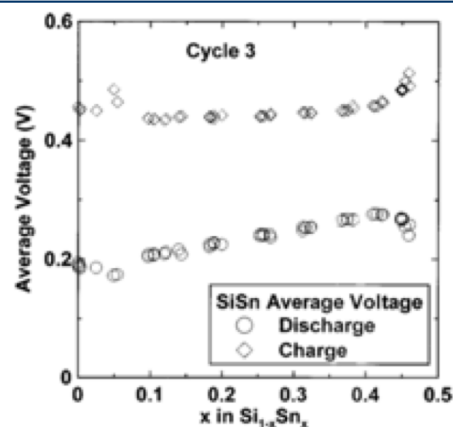


Non-linear increase in conductivity at low concentrations of linear carbonate indicates transport influenced by complex solvation behavior.

Fig. 1. Conductivity of PC and DMC solutions versus the salt concentration.

# Relevance – Novel Alloy Anode Materials

Si anodes suffer from high volumetric expansion, low coulombic efficiency, and continuous SEI growth.



Voltage and irreversible capacity of  $\text{Si}_{1-x}\text{Sn}_x$  films from combinatorial study<sup>[1]</sup>

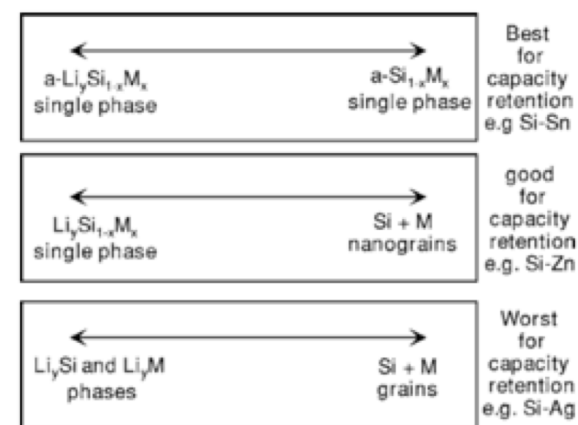


Illustration of structure changes related to capacity behavior<sup>[2]</sup>

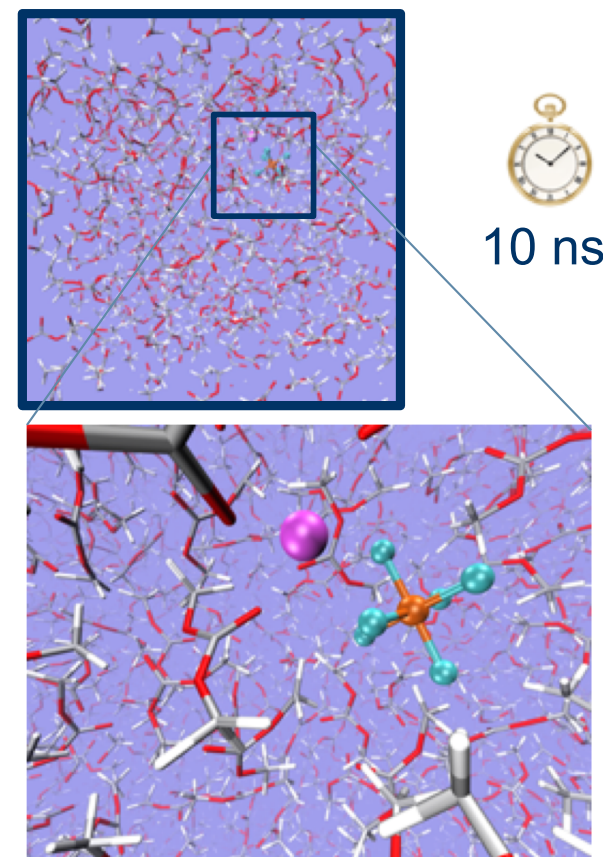
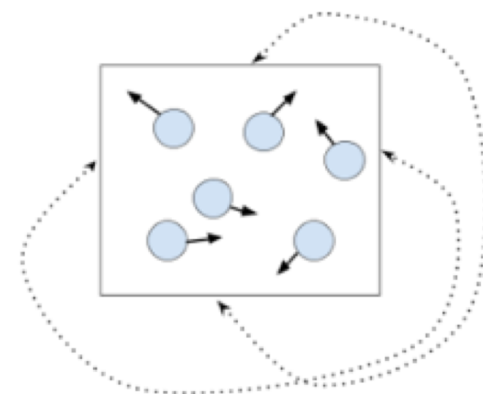
## Objectives:

- Examine the structural evolution of Si alloys; amorphous solid solution vs phase separation
- Identify Si alloy anode materials combining high capacity of Si with favorable properties of other conversion anodes
  - i.e. higher diffusivity, lower voltage, higher volumetric expansion

(1) Hatchard, T. D.; Dahn, J. R. Study of the Electrochemical Performance of Sputtered  $\text{Si}_{[1-x]}\text{Sn}_{[x]}$  Films. *J. Electrochem. Soc.* **2004**, 151 (10), A1628.  
 (2) Hatchard, T. D.; Obrovac, M. N.; Dahn, J. R. A Comparison of the Reactions of the SiSn, SiAg, and SiZn Binary Systems with L3i. *J. Electrochem. Soc.* **2006**, 153 (2), A282.

# Approach (1): Classical Molecular Dynamics

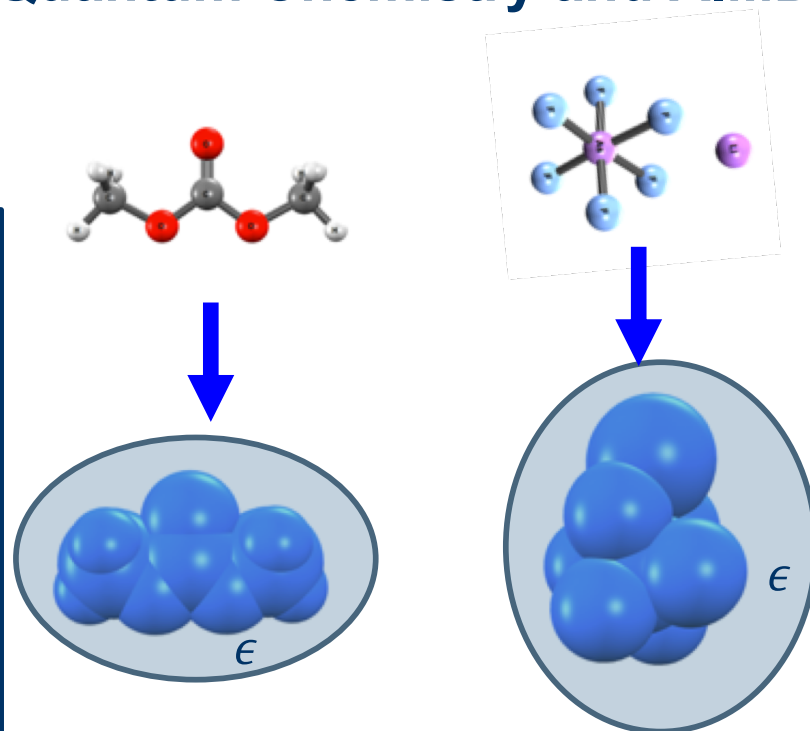
- Classical point charges interacting with each other via a (heavily) parametrized potential
- Periodic boundary conditions
- Maxwell-Boltzmann statistics set temperature and velocity of particles; system evolves in time → thermodynamic observables
- ***No quantum effects, but can treat tens of thousands of atoms***
- ***Good for obtaining solvation structure in complex electrolytes***



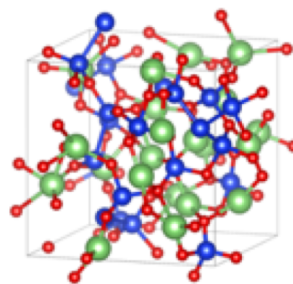


## Approach (2): First Principles Calculations: Quantum Chemistry and AIMD

- Solving Schrodinger's equation (approximately) for  $E_{\text{electronic}}$  (gas phase)
- Free energy is  $F = E_{\text{electronic}} - TS$ . If  $S$  can also be calculated, then  $F$  is known for a compound.
- For compounds in a liquid, can approximate solvent with a surrounding dielectric medium (electrostatic corrections); polarizable continuum model (PCM)
- **Good for obtaining molecular reactivities, voltages**



Ab-initio Molecular dynamics and DFT were used to generate amorphous-like structures in a melt-quench process



Functional	ENCUT
GGA+U	400 eV

System: Periodic Boundaries  
~100 atoms / unit cell

Melt @  
3000K



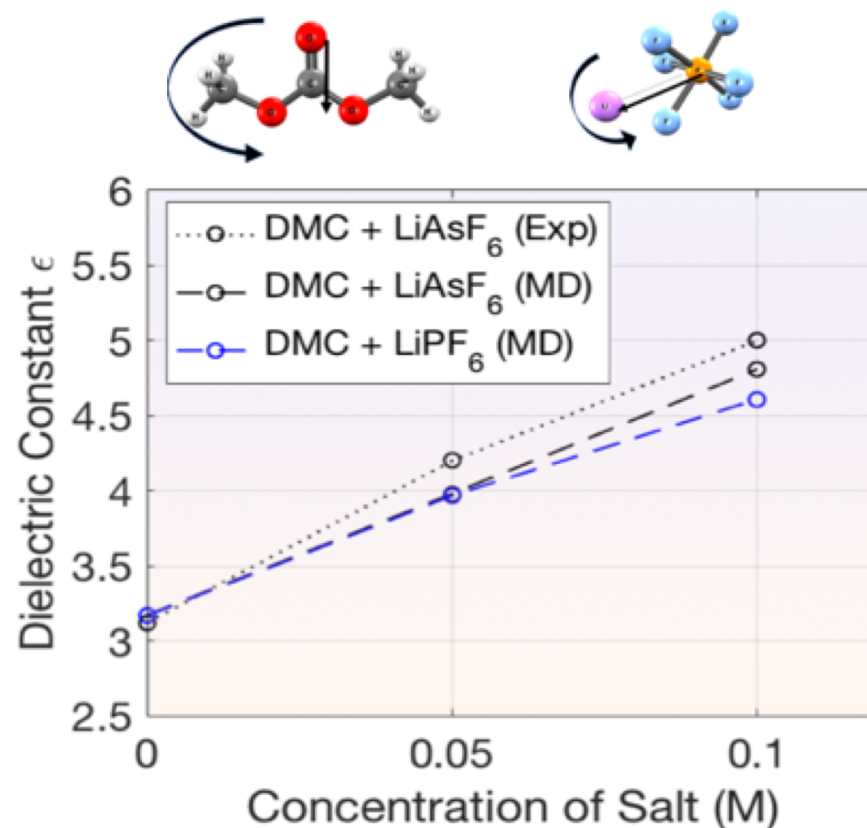
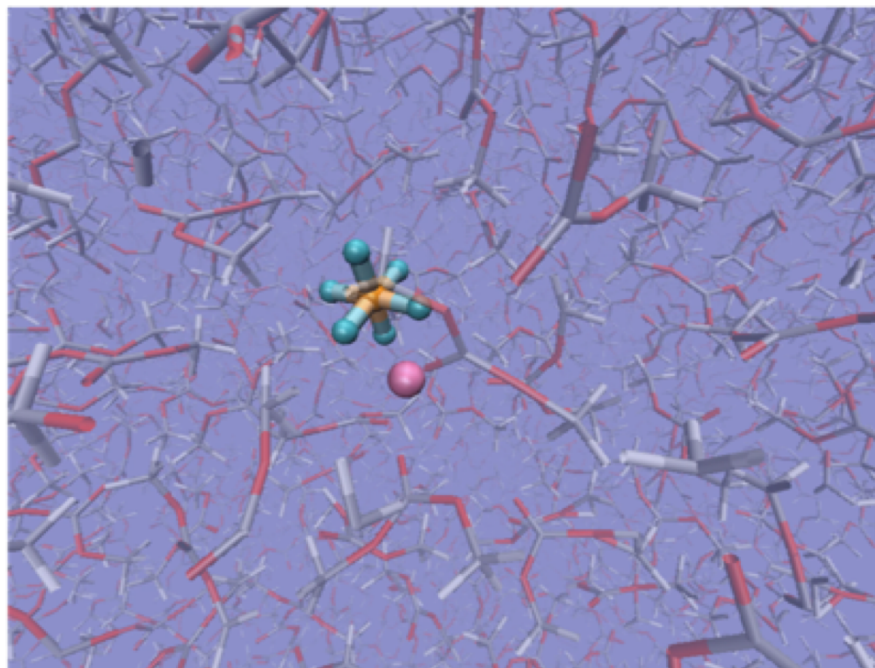
Quench to  
500K



Structure Optimization  
& Energy Calculation

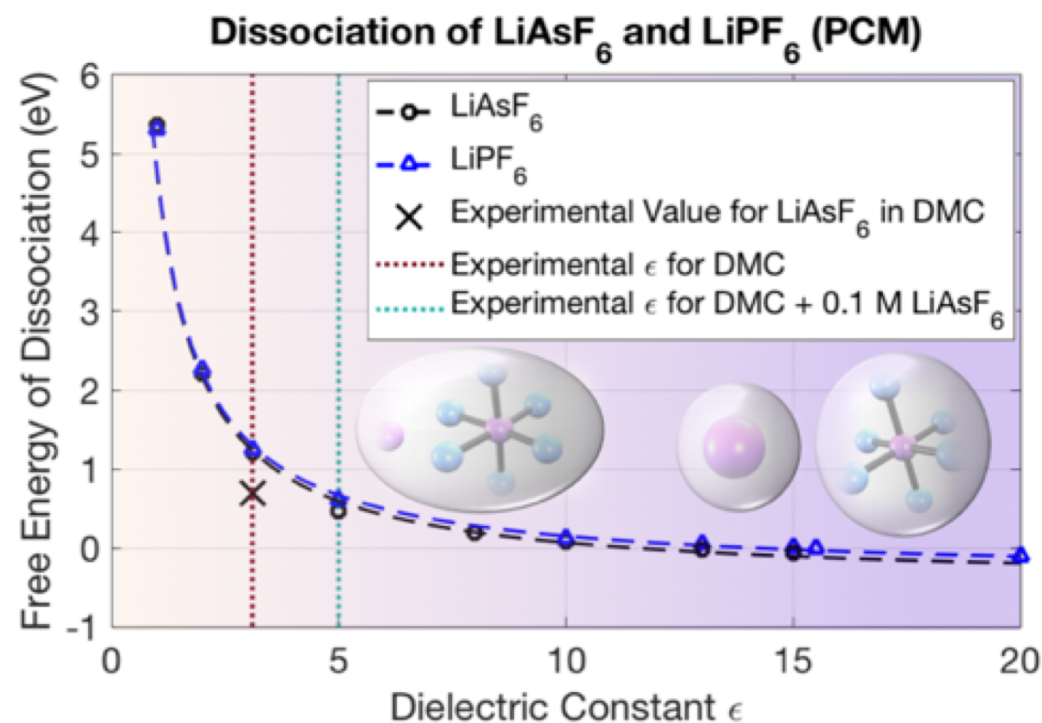
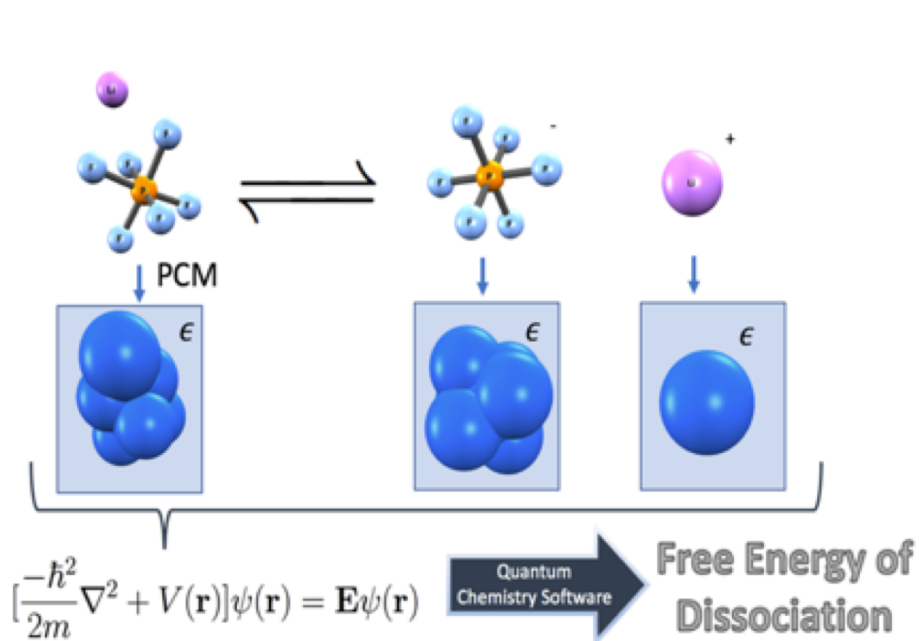
## Accomplishments (1): Contact Ion-Pairs Increase Permittivity of overall Electrolyte

$$\epsilon - 1 \propto (\langle P^2 \rangle - \langle P \rangle^2)$$



- Contact-ion pairs are the majority species at low concentrations of LiAsF<sub>6</sub> as well as LiPF<sub>6</sub> in DMC.
- These contact ion pairs have large dipole moments (much larger than well solvated species) which increases the overall dielectric constant of the composite electrolyte.
- Higher dielectric constant of the electrolyte enables dissolution of more salt, and formation of solvated species (Li<sup>+</sup> and PF<sub>6</sub><sup>-</sup>/AsF<sub>6</sub><sup>-</sup>) which increases the conductivity non-linearly.

## Accomplishments (2): Prediction of concentration limit

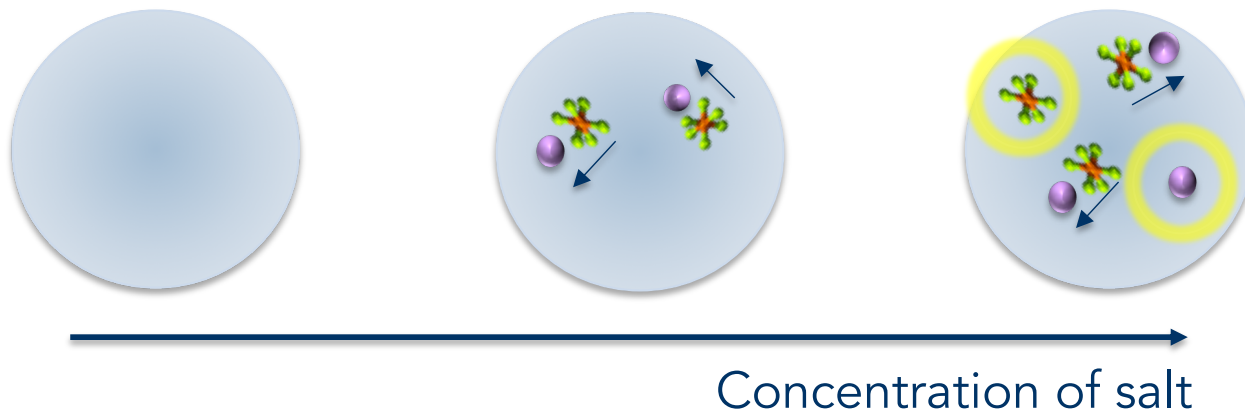


- Calculations enable prediction of the concentration limit for dissociation of contact-ion pairs, resulting in solvated ions and improved conductivity.

## Accomplishments (3): Impact on Salt Dissociation Constant Elucidated

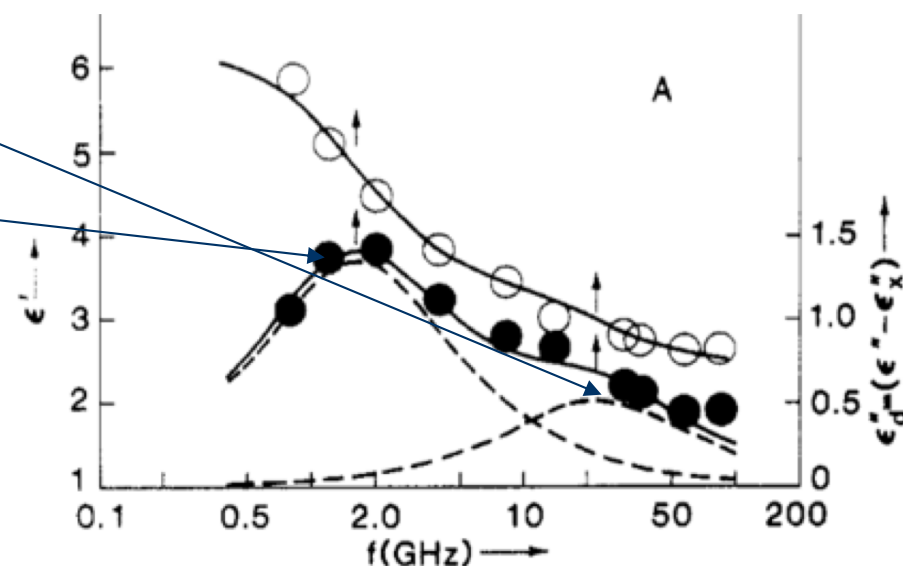
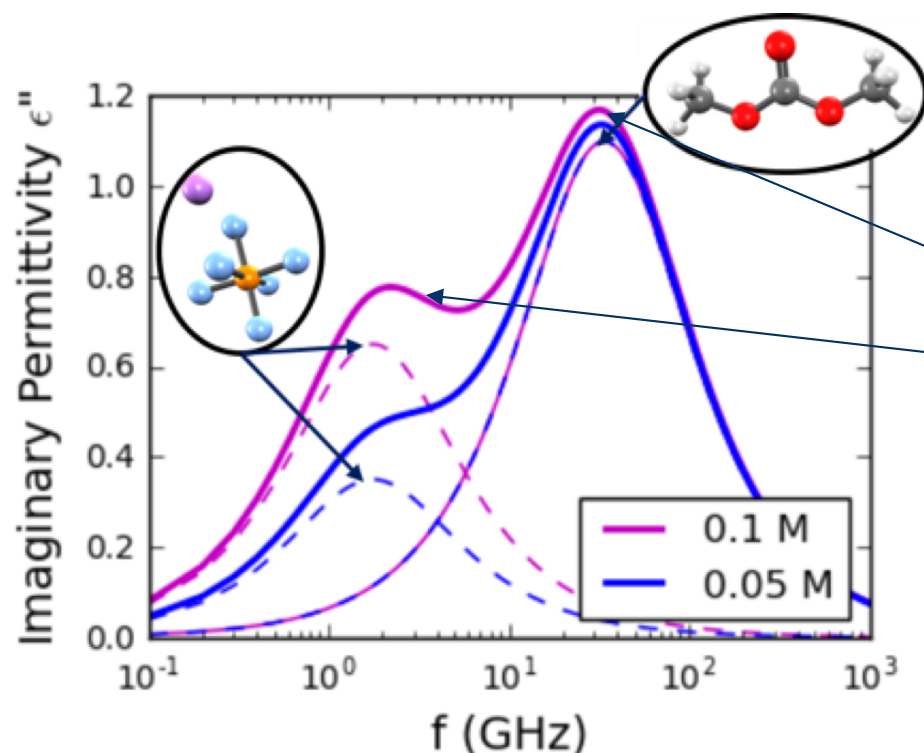
Salt Concentration in DMC	$\geq 0$ M	0.05 M	0.1 M
Calculated $\epsilon$ for $\text{LiPF}_6$	3.2	4.0	4.6
Calculated dissociation $\text{LiPF}_6$	$2.0 \times 10^{-22}$	$2.4 \times 10^{-16}$	$1.7 \times 10^{-13}$

$$K_d = \frac{[\text{Li}^+][\text{PF}_6^-]}{[\text{LiPF}_6]} = \exp(-F_{\text{diss}} / k_B T)$$



- Calculated dielectric constants agree well with available experiments
- Dramatic improvement in electrolyte dielectric constant and dissociation constant explained and quantified

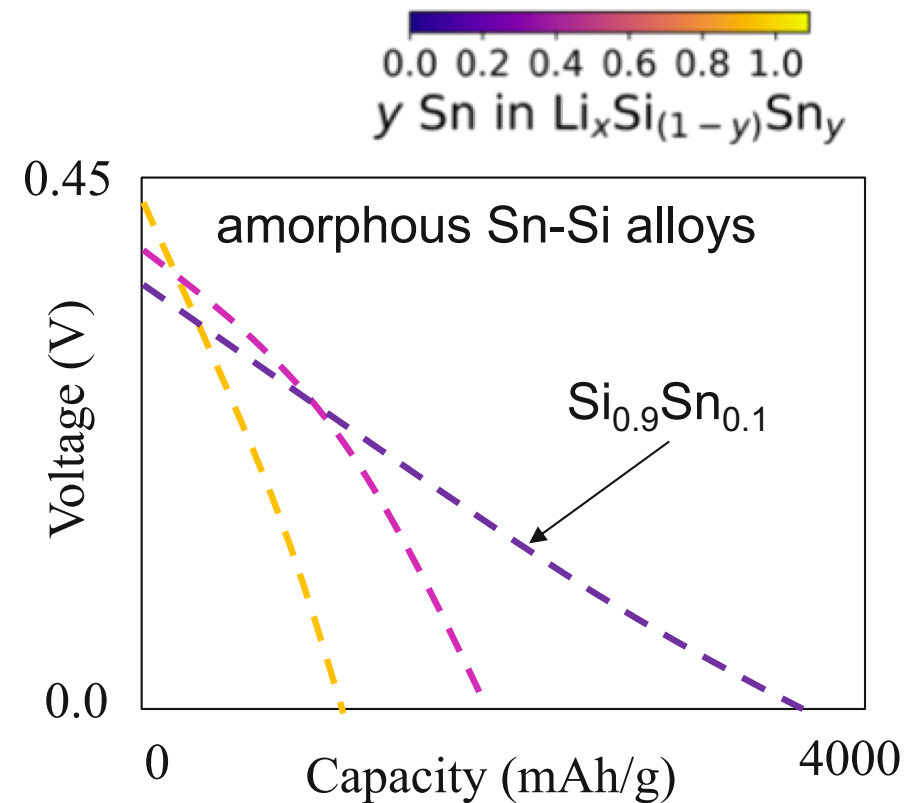
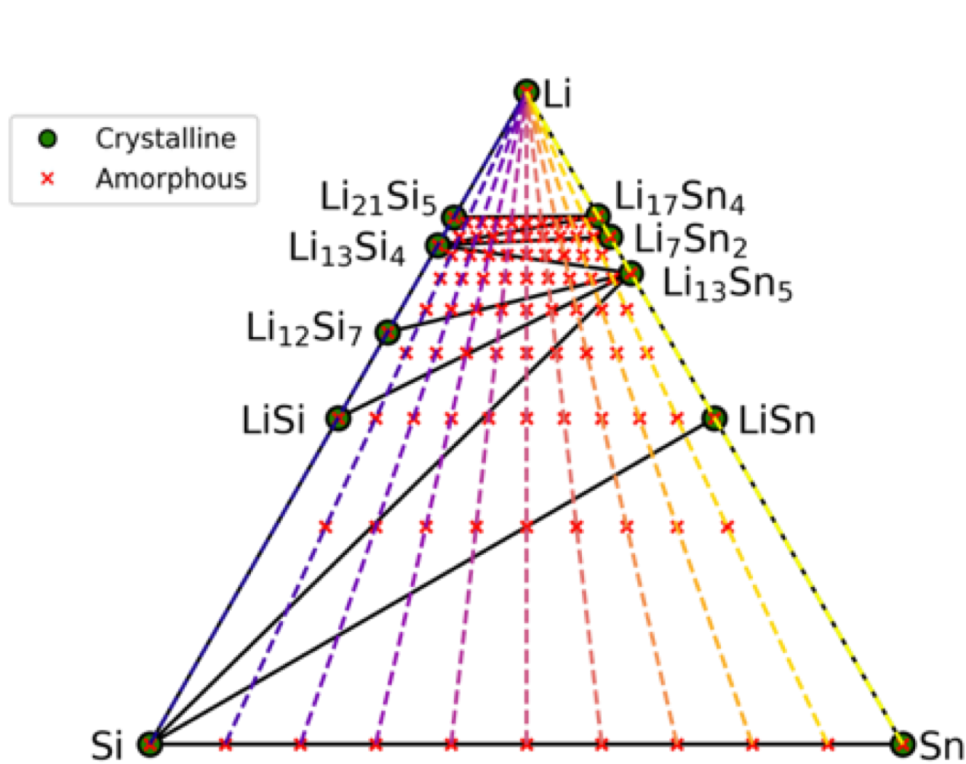
## Accomplishments (4): Prediction of Dielectric frequency signatures



- Developed a framework to provide frequency dependent dielectric signatures of various moieties, both associated salt and solvent in liquid phase.
- Can be used to compare with experimental microwave spectroscopy (dielectric relaxation) to deconvolute the response from many electrolyte species.

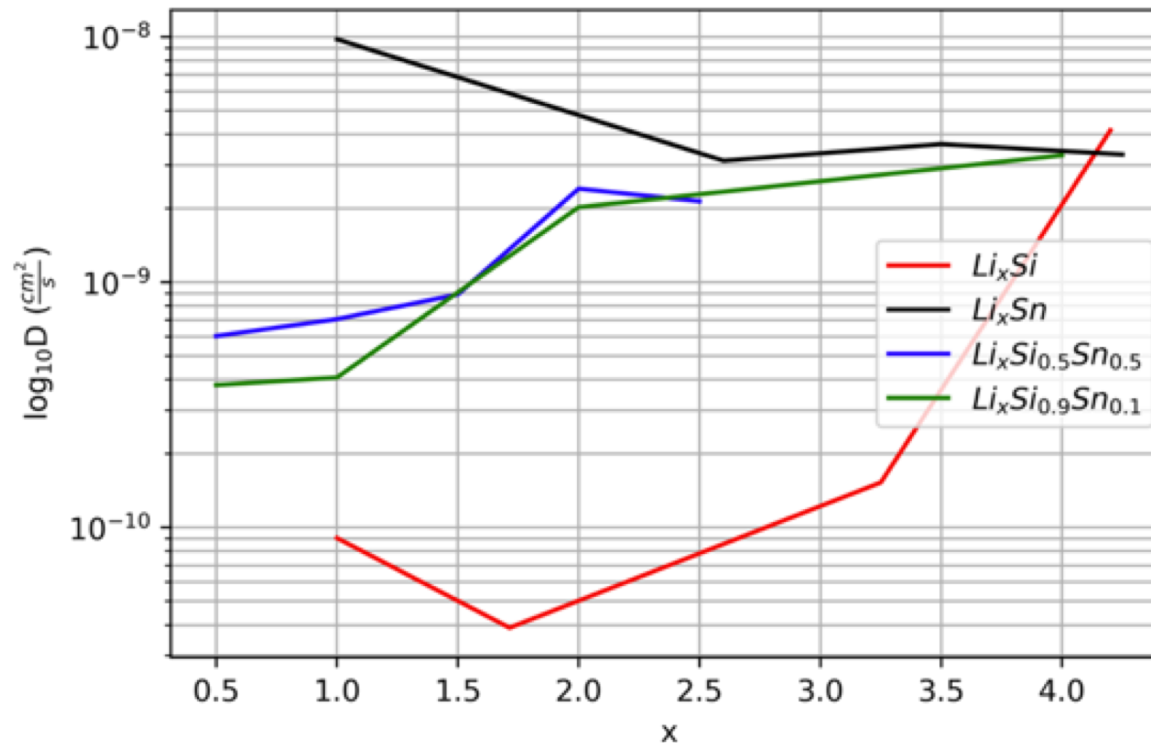


## Accomplishments (5): Phase Diagram and formation energies of Li-Si-Sn alloys



- Amorphous alloys are metastable as compared to the crystalline counterparts
- Higher Sn content amorphous alloys lithiate at slightly higher potential than Si counterparts
- Final gravimetric capacity of higher Sn content electrodes is lower
- Formation energies decrease with Sn content.

## Accomplishments (6): Li Diffusivity in amorphous $\text{Li}_x\text{Si}_{1-y}\text{Sn}_y$



- Li diffusivity in amorphous Sn is 100x greater than amorphous Si, for  $\text{Li} < x$  in  $\text{Li}_x\text{M}$  ;  $\{\text{M}=\text{Si or Sn}\}$
- Addition of small quantities of Sn can have large impact on Li-mobility, improving rate capability in the bulk electrode

# Conclusions

## Low Permittivity Electrolytes

- Associated salt (e.g. contact-ion pairs) can dramatically increase dielectric constant of low permittivity electrolytes as a function of concentration
- Shift in equilibrium of associated to dissociated (charge carrying) salt species as a function of dielectric constant is well inferred from quantum chemical calculations
- Simulations show the critical role that associated salt species plays in non-linear conductivity regimes, and the **predictive nature of the calculations can be used to design linear carbonate electrolytes with higher conductivity**
- Dielectric signatures of salt and solvent species provide a validation tool to be used with spectroscopic measurements to identify the electrolyte species in solution.

## High Li mobility alloy anodes

- Electrode potential is tunable by varying Si-Sn ratio
- Li-Diffusivity in amorphous  $\text{Li}_x\text{Sn}$  is  $\sim 100\times$  greater than  $\text{Li}_x\text{Si}$  at low Li fraction
- Addition of small quantities of Sn can have large impact on Li-mobility
- **Calculations are used to screen for optimal Si alloys with improved bulk as well as surface Li diffusion and thermodynamic properties.**

# Future Work

## Low Permittivity Electrolytes

- Understand interaction of salt association and dielectric properties for different salts and solvents used with low permittivity electrolytes.
- Can use framework to screen for possible binary salt mixtures to be used with low-permittivity electrolytes.

## High Li mobility alloy anodes

- Calculate possible alloying components of Si to improve Li diffusion and electrolyte-surface oxide reactivity
- Model the  $\{\text{Sn}, \text{Si}\}\text{O}_2$  surface of Si-Sn alloy anodes
- Evaluating performance of alloy/conversion electrodes other than Si-Sn.

# Partners and Collaborations

We have existing collaborations in electrolyte work with Bryan McCloskey at LBNL/UC Berkeley as well as initiating more work with Brett Lucht at University of Rhode Island

The Si bulk electrode work is performed in complete synergy and transparency with Brian Cunningham's SEista program, where the Si surface-interface and bulk electrolyte are modelled.





# Previous Review

Presentation ID	Presentation Title	Principal Investigator (Organization)	Page Number	Approach	Technical Accomplishments	Collaborations	Future Research	Weighted Average
es091	Predicting and Understanding Novel Electrode Materials From First-Principles	Kristin Persson (LBNL)	3-55	3.17	3.67	3.00	3.00	3.38

- The reviewer found the PI's scientific abilities and techniques to be of the highest quality and the work is excellent. The reviewer found the PI's willingness to propose solutions to improve performance very impressive.
- The reviewer said that the predicted surface dopants are a nice accomplishment that provided new material design directions on how to stabilize high-capacity Li-excess NMC cathode materials. This is highly relevant and important for meeting DOE energy density goals.
- The reviewer stated that it seems clear that the interfacial properties of the cathode materials in relevance to the bulk, the interactions with the electrolyte species (including solid electrolyte interphase), and the surface coating materials and their migration into the near surface region or dissolution are very complicated phenomena even for experimentalists to gain sufficient understanding from the experimental results. The challenge is much higher for modeling efforts. It is not clear if this first-principles approach is the right approach to deal with this technical area of interest or not. Without a clear justification why this approach will provide a reasonable outcome, it is almost impossible to see if a goal can be established with a reasonable expectation.
- More external collaboration with other theorists and experimentalists is encouraged to gain access to a broader research community for inputs and reliable data to validate the approach. The reviewer found that good collaborations exist.
- If the transport in the bulk regions is good, then one may naturally assume that the transition regions may be a problem. Eliminating these regions may be overlooking an issue, and in fact one result of this study is that the surface phenomena are an issue. The reviewer encouraged the investigator(s) to collaborate with more experimentalists and theorists to develop a more detailed model framework to overcome the current barriers within the model for more fruitful outcomes that can benefit the research community.
- The reviewer commented that extensive modeling work was performed to systematically screen surface doping atoms that can increase oxygen retention on the surface of  $\text{Li}_2\text{MnO}_3$  and asked if there is any plan to valid the model prediction experimentally.
- The reviewer remarked that this research is very much related to petroleum displacement as it will help to enable higher energy batteries.
- The reviewer stated that surface coating and experimental work related to the characterization of any effects is quite difficult to reproduce, and that many of these effects might not be straight to chemical nature. It is not comprehensive how this first-principles approach will resolve these possible variations that may render inconclusive results to conform to a universal understanding in first principles. Defects and amorphous state(s) could be even more challenging to model. It is not clear how these issues will be resolved and modeled with sufficient clarity and fidelity.